Table 1: ^{13}C-nmr data of compound-1,2,6

Carbon No.	δ (ppm)		
	1	2	6
2	165.2	166.39	162.78
3	103.87	103.9	102.98
4	182.9	183.91	181.76
5	153.4	163.26	161.12
6	133.5	100.18	99.42
7	160.64	166.15	164.52
8	92.28	95.05	94.69
9	152.5	159.46	156.81
10	114.26	105.33	105.28
1′	123.58	123.73	121.14
2′	116.84	114.19	113.49
3′	145.6	147.1	145.74
4′	150.21	151.05	150.02
5′	120.48	116.62	116.07
6′	123.58	120.33	119.07
C-6-OCH_3	57.04	-	-
C-7-OCH_3	61.12	-	-
7-O-glucose	-	-	-
1″	-	-	99.83
2″	-	-	73.01
3″	-	-	76.2
4″	-	-	69.5
5″	-	-	75.47
6″	-	-	65.94
7-O-rhamnose	-	-	-
1‴	-	-	100.41
2‴	-	-	70.19
3‴	-	-	70.67
4‴	-	-	71.97
5‴	-	-	68.21
6‴	-	-	17.68

ion peak (M^+) at m/z = 300 (60%) which constituted with the molecular formula $C_{16}H_{12}O_6$. The presence of methoxy group at ring B was confirmed by thr fragment $B1^{\cdot +}$ at m/z = 148.

Finally, the chromatographic and the available spectroscopic data substantiated that compound-3 is chrysoeriol (17).

Xanthomicrol: The UV absorption data confirm the presence of free OH group at C-4' with absence of *ortho*-dihydroxy system and no free OH group at C-7.

The EI-mass spectrum of compound-4 showed a molecular ion peak ($M^{+)}$ at m/z = 344; 6.3% which correspond to the molecular formula $C_{18}H_{16}O_7$. The presence the three methoxy groups at ring-A was confirmed through the presence of the fragment A^+_1 (226) and the fragment at m/z = 118 ; 15.3% .So, we can tentatively identify compound-4 as Xanthomicrol

Apigenin 6, 8-di-O-glucoside: The chromatographic behavour of compound-5 showed, it is aglycosidic in nature. The uv absorption data indicates the presence of a free OH group at C-4' and C-7.

The ^{1}H-nmr revealed the presence of two anomeric protons on ring- A and the other data were coincided with that reported for apigenin (19). After acid hydrolysis, apigenin was isolated as an aglycone and glucose was detected as sugar. The (+ve) FAB/MS of the aglycone of compound-5 displayed a molecular ion peak at m/z = 271 corresponding to the molecular formula of $C_{15}H_{10}O_5$ +1 which coincided with that of apigenin. So, compound-5 can be identified as apigenin 6, 8-di-*O*-glucoside.

Luteolin-7-O-rutinoside: The behaviors of compound-6 in different solvents indicate it is highly glycosidic compound. The UV spectra of compound-6 showed band-I in methanol at 344 nm which proves the flavone nature of this compound.

A bathochromic shift (56 nm) in band-I was noticed upon addition of NaOMe without decreas in intensity indicates the presence of a free OH group at C-4'.

The presence of an *ortho*-dihydroxy system was proved where there is a hypsochromic shift (35 nm) in band-I of $AlCl_3$ spectrum relative to $AlCl_3$/HCl spectrum, also there is a bathochromic shift (16 nm) in band-I of NaOAc/H_3BO_3 spectrum relative to methanol spectrum.

The absence of free OH group at C-7 was confirmed where there is no bathochromic shift in band-II of NaOAc spectrum.

The ^{1}H-nmr data were in accordance with that reported for luteolin 7-*O*-rutinoside.

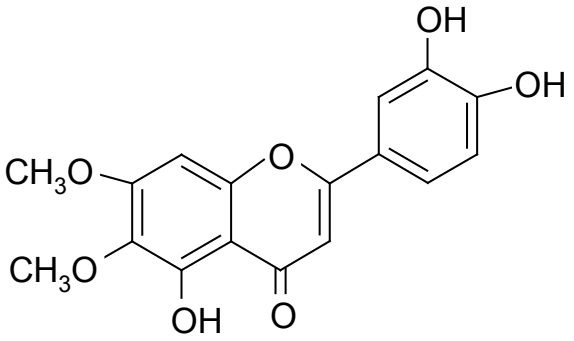
The ^{13}C-nmr spectrum (DMSO) of compound-6 showed the most characteristic signals of flavone diglycoside like C-4 at δ = 181.76, C-1" at 99.83, C-1‴ at 100.41 and C-6‴ of CH_3 group of rhamnose at 17.68. The down filed shift of C-6" (65.94) and C-1‴ (100.41) indicates the two sugars are rutinoside i.e. gluco-(61) rhamnoside (20) and in accordance with those of luteolin-7-*O*-rutinoside. The other data of ^{13}C-nmr were found in table (1).The acid hydrolysis revealed the presence of glucose and rhamnose were detected as sugars and luteolin as an aglycone.

The position of the attachment of these sugars to the aglycone was confirmed at C-7 where the UV spectra of the aglycone showed a bathochromic shift in band-II in NaOAc spectrum relative to methanol spectrum. Also the identity of luteolin was confirmed by the +ve FAB/MS, where it displayed a molecular ion peak at m/z = 287.

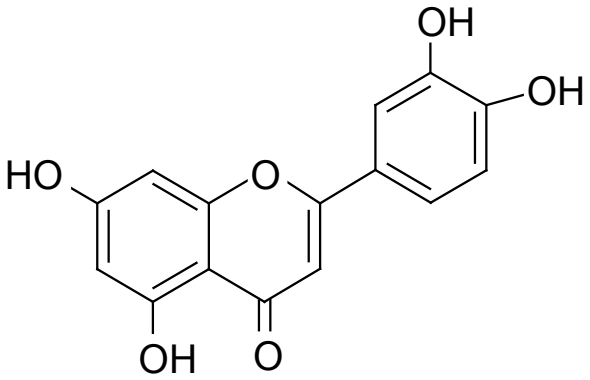
From all the above chromatographic and spectroscopic data, we can identify compound-6 as Luteolin-7-*O*-rutinoside. All these compounds were isolated for the first time from this species.some of it were isolate from other Teucriumspecies like cirsiolol, luteolin, luteolin 7-O-rutinoside, apigenin di glucoside (8, 21–25).

INSECTICIDAL ACTIVITY:

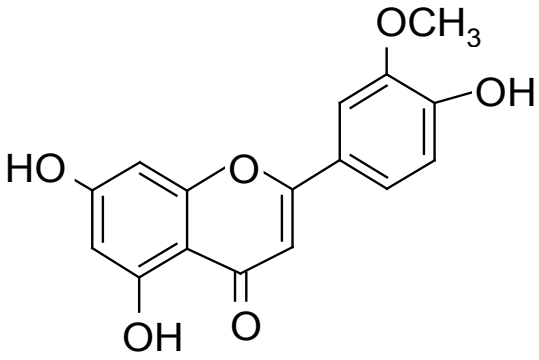
The results in table (2) indicated that, all extracts used proved to have various degrees of insecticidal effect on the adult beetles. There is significance between aqueous



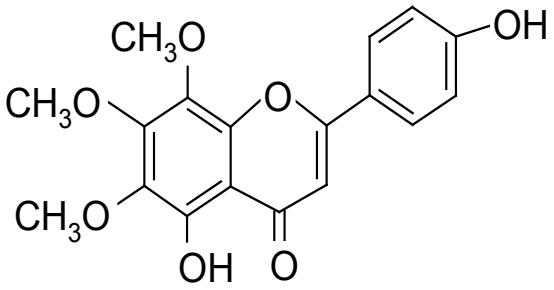
Cirsiliol



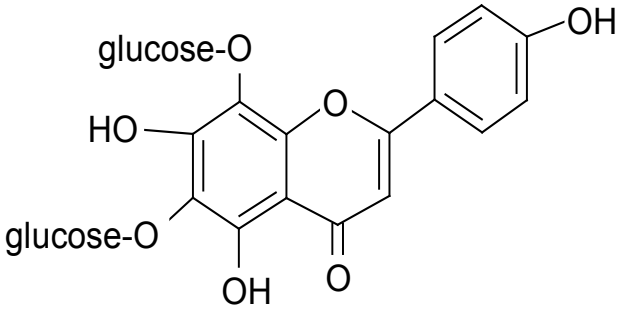
Luteolin



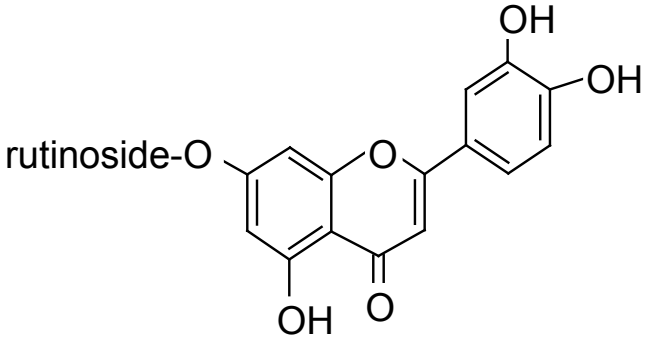
Chrysoeriol



Xanthomicrol



Apigenin 6,8-di-O-glucoside



Luteolin-7-O-rutinoside

and alcoholic extracts. These results clarify that aqueous extract was the most efficient as insecticide followed by alcoholic extract which may be due to the most active compounds like diterpenoids and flavonoids were found in both extracts (26).

Filed experiments results (table 3) of insecticidal activity show that the mean numbers of *P. oleae* Fab. on the olive trees before treatments, ranged from 13:00 to 15:00, indicating a relatively uniform distribution of insect infestation. One week after spraying, the treatments suppressed the levels of infestation to different degrees compared to that of untreated control. Aqueous, alcoholic and butanol extracts significantly lowered the percentage of infestation to 70.82%, 65.86% and 66.56%, respectively. Two weeks post-treatment, aqueous extract become more efficient and had almost similar activity as cidial 50% (conventional chemical insecticides, unpublished data) displaying 71.39% and 73.9% reduction in infestation respectively. Similar results were reported by Ismail and Abdalla (13).

As for the 3rd week after the treatment, both aqueous extract and alcoholic showed good bioresidual activities against *P. oleae* giving 72.63% and 62.07% reduction, respectively. This was in accordance with Masanori *et. al.* in

2000(27), they reported that some methoxylated flavones have antifeedant activity. So the insecticidal activity of T. zanonii may be due to the presence of such compounds in the active extracts. Accordingly, the present study showed that *T. zanonii* extracts was a good candidate to be considered for protecting olive trees against this pest in integrate pest management (IPM) program (28).

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